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DETERMINATION OF CHROMIC ACID IN CHROMIUM PLATING SOLUTIONS USING A REDOX TITRATION AND INDICATOR

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The chemical literature lacks a simple analytical method for adequately controlling chromic acid in chromium plating solutions during the plating process. In this report, a simple method for analyzing and controlling chromic acid during the plating process is presented. The optimum operating range of chromic acid is 240 to 260 g/l and the resulting precisions are in the range of 0 to 2.5 g/l, providing adequate control of these plating solutions supported by five years of testing.

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TABLE OF CONTENTS

TABLES

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INTRODUCTION

The chemical literature lacks a simple analytical method for adequately controlling chromic acid in chromium plating solutions during the plating process. Lack of optimization of these plating solutions causes serious problems for the chromium plating industry such as poor quality products, wasted human resources, and wasted electrical energy.

A quick general analytical method to determine chromic acid in chromium plating solutions is to use a Baume hydrometer and to assume that all of the dissolved material is chromic acid (ref 1). However, the problem with this density method is that it not only measures chromic acid, but all dissolved material and must be corrected for temperature. It is not uncommon for this method to deliver relative precisions in the range of 5 to 10 percent for these chromic acid measurements.

Another chemical analysis method to determine chromic acid in chromium plating solutions is to use atomic absorption or inductively coupled plasma spectrometry and to assume that all chromium is in the form of chromic acid (ref 2). The problem with this method is that Cr(III) ions are also present in these solutions and must be corrected by a separate Cr(III) ion analysis method. Relative precisions of the combined methods are in the range of 3 to 5 percent.

Still another chemical analysis method to determine chromic acid in chromium plating solutions is sodium thiosulfate titration using a potassium iodide/starch indicator (refs 3-5). This method is time-consuming since the sodium thiosulfate is unstable and must be standardized every time it is used, although after standardization relative precisions are in the range of 1 to 2 percent.

References are listed at the end of this report.

The simple method given in this report provides both acceptable analysis and control of chromic acid in chromium plating solutions. The method uses a ferrous ammonium sulfate redox titrant and redox indicator. General background on redox titration is extensive (refs 2-6).

EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental procedure section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 6).

One analytical reagent grade standard solution is required. This solution is a 4.90 ± 0.01-g/l potassium dichromate solution that meets American Chemical Society (ACS) Standards and Federal Specification O-C-303D for hexavalent chromium (refs 7-8).

Two other reagent grade solutions are required. The first of these is the redox titrant which has 45.0 ± 0.01 grams of ferrous ammonium sulfate (six hydrate) and 60 ± 1 milliliters (ml) of sulfuric acid per liter of total solution. The second is the redox indicator which is a 10.0 ± 0.1-g/l sodium diphenylamine sulfonate solution.

Preparation of a potassium dichromate standard for redox titration analysis requires that 25 ml of the analytical reagent grade standard solution prepared above is diluted to about the 200-ml mark with deionized water in a 400-ml beaker. In addition, 5 ml of concentrated sulfuric acid, 5 ml of concentrated phosphoric acid, a stirring bar, and five drops of the redox indicator are added to the beaker. The redox titrant is titrated to a green endpoint recording the amount of titrant dispensed.

Preparation of a chromium plating solution sample for redox titration analysis requires that 10 ml of the sample solution is pipetted into a 500-ml volumetric flask which is filled to the mark with deionized water. Then 25 ml of the diluted sample solution in the flask is diluted to about the 200-ml mark with deionized water in a 400-ml beaker. As before, 5 ml of concentrated sulfuric acid, 5 ml of concentrated phosphoric acid, a stirring bar, and five drops of the redox indicator are added to the beaker. The redox titrant is titrated to a green endpoint recording the amount of titrant dispensed.

All standard and sample solutions are analyzed in triplicate. Chromic acid concentrations in the samples are calculated by simple proportion.

RESULTS AND DISCUSSION

Experimental redox titration data are presented in Table I for the potassium dichromate standard solution and in Table II for the chromic acid sample solutions one and two. The redox titration consists of the following:

$$(Cr_2O_7)^{2-} + 6(Fe)^{2+} + 14(H)^{+} \text{ <--> } 2(Cr)^{3+} + 6(Fe)^{3+} + 7(H_2O) \quad (1)$$

All hexavalent chromium is in the dichromate form due to the addition of sulfuric and phosphoric acids added to the standard and sample solutions above.

Theoretically, from Eq. (1), it is calculated that a 21.77-ml volume of the titrant at the endpoint is required for the standard solution which is the value experimentally obtained in Table I.

Although all standards and samples are analyzed in their dichromate form, all samples are actually in the chromate form and are reported as chromium trioxide using the following equations for conversion:

$$(Cr_2O_7)^{2-} + 2(OH)^- \leftrightarrow 2(CrO_4)^{2-} + H_2O \quad (2)$$

$$(CrO_4)^{2-} + 2(H)^+ \leftrightarrow CrO_3 + H_2O \quad (3)$$

From Eqs. (2) and (3), it is found that the sodium dichromate standard solution has the equivalent of 245 g/l potassium dichromate or 166.55 g/l chromium trioxide (CrO_3).

Therefore, by simple proportion, the calculation for determining the concentration of chromium trioxide in the sample solutions is:

$$g/l\ CrO_3 = (166.55)\ (\text{titrant ratio}) \quad (4)$$

where the titrant ratio is the milliliter of sample titrant used divided by the milliliter of standard titrant used.

From Eq. (4), the values of 244.2 and 255.5 g/l chromium trioxide are respectively calculated for sample solutions one and two for the data given in Table II.

It is useful to evaluate the variations in precision for the materials and methods used. Tables III through VII present these data for the 25-ml class-A pipets, 10-ml class-A pipets, 500-ml class-A volumetric flasks, 50-ml class-A burets, and the 4.90-g/l potassium dichromate standard solution, respectively.

The data obtained by this method are sufficient to adequately control the chromic acid in the Watervliet Arsenal's chromium plating processes according to its standard operating procedures (ref 9), thus providing efficient use of resources. The optimum operating range of chromic acid is 240 to 260 g/l and the resulting precisions are in the range of 0 to 2.5 g/l, providing adequate control of these plating solutions supported by five years of testing.

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TABLE I. EXPERIMENTAL REDOX TITRATION DATA FOR THE POTASSIUM DICHROMATE STANDARD SOLUTION

Replicate	Titrant Used (ml)
1	21.80
2	21.75
3	21.75
X(avg)	21.77

TABLE II. EXPERIMENTAL REDOX TITRATION DATA FOR THE CHROMIC ACID SAMPLE SOLUTIONS

Replicate	Sample One Titrant Used (ml)	Sample Two Titrant Used (ml)
1	31.95	33.40
2	31.90	33.40
3	31.90	33.40
X(avg)	31.92	33.40

TABLE III. PRECISION OF A 25-ml CLASS-A PIPET

Replicate	Volume (ml)*
1	25.04
2	24.99
3	24.96
4	25.03
5	25.01
6	25.05
X(avg)	25.01
Sn	0.03

TABLE IV. PRECISION OF A 10-ml CLASS-A PIPET

Replicate	Volume (ml)*
1	10.03
2	10.00
3	9.98
4	9.99
5	9.98
6	10.04
X(avg)	10.00
Sn	0.02

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE V. PRECISION OF A 500-ml CLASS-A VOLUMETRIC FLASK

Replicate	Volume (ml)*
1	500.6
2	500.1
3	499.8
4	500.0
5	500.5
6	499.3
X(avg)	500.1
Sn	0.4

TABLE VI. PRECISION OF A 50-ml CLASS-A BURET

Replicate	Volume (ml)*
1	24.94
2	24.98
3	25.02
4	25.05
5	24.98
6	25.05
X(avg)	25.00
Sn	0.04

*Volumes are calculated from the weight-volume relationship of a contained deionized water solution corrected for temperature.

TABLE VII. PRECISION OF A 4.90-g/l POTASSIUM DICHROMATE STANDARD SOLUTION BY TITRATION

Replicate	$K_2CR_2O_7$ Conc. (g/l)*
1	4.91
2	4.88
3	4.90
4	4.89
5	4.91
6	4.91
X(avg)	4.90
Sn	0.01

*Potassium dichromate as chromic acid concentrations are calculated using Federal Specification O-C-303D which is a standard chemical analysis method for chromic acid.

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